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For: METHOD OF OPERATING FUEL CELL SYSTEM AND FUEL CELL SYSTEM AND FUEL SYSTEM

TRANSMITTAL OF VERIFICATION OF ENGLISH TRANSLATION OF CERTIFIED PRIORITY DOCUMENT

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Sir:

Transmitted herewith is a Verification of English translation of the Japanese priority document JP 2002-317794, filed October 31, 2002.

To the extent necessary, a petition for an extension of time under 37 C.F.R. 1.136 is hereby made. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account 500417 and please credit any excess fees to such deposit account.

Respectfully submitted,

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Certificate

I, the undersigned, Keiji HABA of c/o Patent Corporate Body ARCO PATENT OFFICE at 3rd Fl., Bo-eki Building, 123-1 Higashimachi, Chuo-ku, Kobe-shi 650-0031 JAPAN, hereby declares that I am conversant with Japanese and English languages and that attached is/are, to the best of my knowledge and belief, a true English translation of the Japanese Patent Application No. 2002-317794.

Dated this 17th day of September, 2009

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[Title of the Invention] METHOD FOR OPERATING FUEL CELL AND FUEL CELL SYSTEM

[Claims]

1. A method for operating a fuel cell comprising an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode,

the method comprising a step of carrying out a restoring operation by decreasing an electric potential of the electrode on an oxygen side, upon decreasing a voltage of the fuel cell to a threshold voltage or lower, or upon lapsing a prescribed period of time from a preceding restoring operation.

2. A method for operating a fuel cell comprising plural cells each containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode,

the method comprising steps of carrying out a restoring operation by decreasing an electric potential of the electrode on an oxygen side of at least one of the plural cells, and after restoring a voltage of the cells, sequentially carrying out

a restoring operation for the other cells.

3. A method for operating a fuel cell as claimed in claim 1 or 2, wherein the restoring operation comprises such an operation that electric power generation is continued while a feeding amount of the oxygen-containing gas on the oxygen electrode is decreased, and after lowering the cell voltage to a restoring voltage of the oxygen electrode (with respect to the fuel electrode), the feeding amount of the oxygen-containing gas is then increased.

4. A method for operating a fuel cell as claimed in claim 1 or 2, wherein the restoring operation comprises such an operation that electric power generation is continued while feed of the oxygen-containing gas is terminated, and after lowering the cell voltage to a restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of the oxygen-containing gas is restarted.

5. A method for operating a fuel cell as claimed in claim 1 or 2, wherein the restoring operation comprises such an operation that an inert gas or a hydrocarbon gas is fed to the oxygen electrode, and after lowering the cell voltage to a restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of the oxygen-containing gas is restarted.

6. A method for operating a fuel cell as claimed in claim 1 or 2, wherein the restoring operation comprises such an operation that water is fed to the oxygen electrode, and after

lowering the cell voltage to a restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of the oxygen-containing gas is restarted.

7. A method for operating a fuel cell as claimed in claim 1 or 2, wherein the restoring operation comprises such an operation that a reducing agent is fed to the oxygen electrode, and after lowering the cell voltage to a restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of the oxygen-containing gas is restarted.

8. A method for operating a fuel cell as claimed in claim 1 or 2, wherein the restoring operation comprises such an operation that a load of the fuel cell is increased, and after lowering the cell voltage to a restoring voltage of the oxygen electrode (with respect to the fuel electrode), the load is decreased.

9. A method for operating a fuel cell comprising an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode,

the method comprising a step of carrying out a restoring operation by decreasing an electric potential of the electrode on an oxygen side, after terminating an operation of the fuel cell.

10. A fuel cell system comprising a stack of cells each containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the fuel cell system further comprising a voltage detecting means for detecting a voltage of the cells or the stack, and a controlling means for controlling the feed of the oxygen-containing gas to the cells or the stack based on the voltage detected by the voltage detecting means.

11. A fuel cell system comprising a stack of cells each containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the fuel cell system further comprising a voltage detecting means for detecting a voltage of the cells or the stack, a feeding means for feeding water to the cells or the stack, and a controlling means for controlling the feeding means based on the voltage detected by the voltage detecting means.

12. A fuel cell system comprising a stack of cells each containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having

a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the fuel cell system further comprising a voltage detecting means for detecting a voltage of the cells or the stack, a feeding means for feeding an inert gas, a hydrocarbon gas or a reducing agent to the cells or the stack instead of the oxygen-containing gas, and a controlling means for controlling the feeding means based on the voltage detected by the voltage detecting means.

13. A fuel cell system comprising a stack of cells each containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the fuel cell system further comprising a voltage detecting means for detecting a voltage of the cells or the stack, an electric current adjusting means for increasing and decreasing an electric current applied to the cells or the stack, and a controlling means for controlling the electric current adjusting means based on the voltage detected by the voltage detecting means.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a fuel cell, and in particular, it relates to a method for operating a fuel cell for restoring deterioration of the output voltage thereof, and a fuel cell system therefor.

[0002]

[Prior Art]

A fuel cell generates electric power through reaction of a fuel gas fed to a fuel electrode and an oxygen-containing gas fed to an oxygen electrode. As the fuel gas, hydrogen supplied from a hydrogen cylinder or a reformed gas obtained by reforming a city gas to enrich the hydrogen content are used. As the oxygen-containing gas, air is generally fed with a compressor or a blower. An electrode of a fuel cell is generally made of an electroconductive carbon having a noble metal carried on the surface thereof.

[0003]

[Problems to be Solved by the Invention]

A catalyst used on the electrode of the fuel cell is gradually oxidized on the surface thereof upon being exposed to an oxidative atmosphere, and adsorbs contaminants in the air and contaminants leaked from the apparatus on the surface of the catalyst. The reaction efficiency of the catalyst is lowered thereby, and thus the generated voltage is lowered with the lapse of time. In order to solve the problem, it has been proposed that in the shutdown period of the fuel cell, an inert

gas, such as a nitrogen gas, is charged to prevent oxidation of the electrodes, and the fed gas is fed through a filter to decrease the amount of contaminants in the gas. However, these measures cannot restore the voltage having been once lowered although the lowering of the generated voltage can be suppressed to prolong the service life. Furthermore, a fuel cell has such a nature that the generated voltage thereof is eventually lowered despite of the effect of prolonging the service life.

[0004]

In the case where the gas is fed through a filter, it is necessary to exchange the filter on a regular schedule to cause such a problem of consuming labor and cost for exchanging the filter. Furthermore, additional energy is necessary in the compressor or the blower corresponding to the pressure loss of the filter.

[0005]

The invention is to solve the aforementioned problems associated with the conventional art, and an object thereof is to provide a method for operating a fuel cell for maintaining a high generated voltage for a long period of time by carrying out a restoring operation for restoring the generated voltage upon decreasing the generated voltage of the fuel cell.

Another object of the invention is to provide a fuel cell system that is constituted to enable the method for operating a fuel cell.

[0006]

[Means for Solving the Problems]

The invention relates to, as one aspect, a method for operating a fuel cell containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the method containing a step of carrying out a restoring operation by decreasing an electric potential of the electrode on an oxygen side, upon decreasing a voltage of the fuel cell to a threshold voltage or lower, or upon lapsing a prescribed period of time from a preceding restoring operation.

The invention also relates to, as another aspect, a method for operating a fuel cell containing plural cells each containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the method containing steps of carrying out a restoring operation by decreasing an electric potential of the electrode on an oxygen side of at least one of the plural cells, and after restoring a voltage of the cells, sequentially carrying out a restoring operation for the other cells.

[0007]

The invention also relates to, as still another aspect, a method for operating a fuel cell containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the method containing a step of carrying out a restoring operation by decreasing an electric potential of the electrode on an oxygen side, after terminating an operation of the fuel cell.

[0008]

The invention also relates to, as a further aspect, a fuel cell system containing a stack of cells each containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, the fuel cell system further containing a voltage detecting means for detecting a voltage of the cells or the stack, and a controlling means for controlling the feed of the oxygen-containing gas to the cells or the stack based on the voltage detected by the voltage detecting means.

[0009]

[Embodiments of the Invention]

A fuel cell is constituted essentially with an electrolyte membrane and electrode disposed on both side thereof. The electrode for a fuel cell is constituted with a gas diffusion layer for feeding a reaction gas and a catalyst layer for actually effecting a chemical reaction. A noble metal catalyst carried on carbon is used as the catalyst layer.

A fuel cell generates electric power by reacting a fuel gas fed to a fuel electrode and an oxygen-containing gas fed to an oxygen electrode. As the oxygen-containing gas, air is generally fed with a compressor or a blower. However, air contains a nitrogen oxide and a sulfur oxide, which deteriorate the electric power generation reaction. Furthermore, members constituting the apparatus leak organic substances, such as a solvent.

These contaminants are gradually accumulated on the surface of the catalyst during the operation of the fuel cell to deteriorate the generated voltage. Most part of the contaminants can be decomposed or removed by changing the electric potential on the surface of the catalyst.

[0010]

The accumulation of contaminants may occur on both the fuel electrode and the oxygen electrode, but the electric potential of the fuel electrode receives less influence of the accumulation of contaminants due to the small overvoltage

thereof. Therefore, the deterioration of the generated voltage occurring on the operation of the fuel cell is mainly ascribed to the accumulation of contaminants on the oxygen electrode.

A noble metal, such as platinum, used as the catalyst is generally hard to be oxidized, but because a fuel cell using a polymer electrolyte is in a strongly acidic atmosphere, the surface of the catalyst is oxidized in the case where the electric potential of the oxygen electrode is high in the fuel cell. The surface of platinum is oxidized in the case where the electric potential of the fuel electrode is 0.7 V or more with respect to the standard hydrogen electrode in a pH range of from 1 to 2. When the surface of the catalyst is oxidized, the rate of the redox reaction of oxygen is decreased, and thus the generated voltage is lowered. Furthermore, since the oxide has a large adsorption power to the contaminants, it promotes the accumulation of contaminants to accelerate lowering of the generated voltage.

[0011]

In order to resolve the accumulation of contaminants and the oxidation on the surface of the catalyst to restore the generated voltage, it is effective to carry out the restoring operation for lowering the electric potential of the oxygen electrode.

In a fuel cell using a polymer electrolyte, the cell voltage upon normal operation under no load is about 0.95 V,

and the cell voltage upon operation with a load is lowered to 0.8 to 0.6 V. The electric potential of the fuel electrode is substantially equal to the electric potential of the standard hydrogen electrode in the case where a hydrogen-containing gas is used as the fuel gas. Furthermore, the electric potential of the oxygen electrode (with respect to the fuel electrode) is substantially equal to the cell voltage owing to the low overvoltage of the fuel electrode. Accordingly, the electric potential of the oxygen electrode can be comprehended by detecting the cell voltage to find completion of the restoring operation. The threshold value of the cell voltage, which is an indication for carrying out the restoring operation of the invention, is preferably 95% of the aforementioned initial voltage. In the case where the threshold value is too high, it is complicated since the restoring operation should be frequently carried out. In the case where the threshold value is too low, on the other hand, there is such a possibility that the electric generation efficiency is lowered, and sufficient restoration cannot be attained.

[0012]

The electric potential where the restoring operation is carried out may be less than 0.7 V (with respect to the fuel electrode) in the case where restoration is attained by reducing the oxidized and deteriorated catalyst. In particular, it is also effective that the fuel cell is electrically shorted out

for several tens seconds. In the case where deterioration due to adsorbed contaminants is restored by reduction and desorption, it is preferably 0.4 V or less (with respect to the fuel electrode). Both the deterioration due to oxidation of the catalyst and the deterioration due to adsorption of contaminants can be resolved by setting the restoring electric potential at 0.4 V (with respect to the fuel electrode).

The restoring operation may be carried out simultaneously to all the cells constituting the stack, or in alternative, it may be carried out for the respective cells one-by-one or for a part of the cells, and then sequentially carried out for other cells. In the case where the restoring operation is carried out simultaneously for all the cells, detection of the voltage of the entire stack can be substituted for the detection of the cell voltage. In the case where the restoring operation is carried out for the respective cells one-by-one, such an advantage can be obtained that the restoring operation can be carried out more certainly, although a complicated constitution of the stack is required for detecting the voltages of the respective cells.

[0013]

Examples of the restoring operation include the following methods. (1) Electric power generation is carried out under such a state that the feeding amount of oxygen is lowered to consume oxygen, (2) a hydrocarbon gas, an inert gas or water

is fed for replacing oxygen, (3) a reducing agent is fed, and (4) the load of the fuel cell is increased. These methods will be described in more detail below.

[0014]

In a preferred embodiment of the invention, the restoring operation contains such an operation that electric power generation is continued while the feeding amount of the oxygen-containing gas on the oxygen electrode is decreased, and after lowering the cell voltage to the restoring voltage of the oxygen electrode (with respect to the fuel electrode), the feeding amount of the oxygen-containing gas is then increased.

In another preferred embodiment, the restoring operation contains such an operation that the electric power generation is continued while the feed of the oxygen-containing gas is terminated, and after lowering the cell voltage to the restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of the oxygen-containing gas is restarted.

[0015]

In still another preferred embodiment, the restoring operation contains such an operation that an inert gas or a hydrocarbon gas is fed to the oxygen electrode, and after lowering the cell voltage to the restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of the oxygen-containing gas is restarted.

In a further preferred embodiment, the restoring operation contains such an operation that water is fed to the oxygen electrode, and after lowering the cell voltage to the restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of water is terminated. During the restoring operation of this method, feed of the oxygen-containing gas may be continued.

[0016]

In a still further preferred embodiment, the restoring operation contains such an operation that an inert gas, a hydrocarbon gas or a reducing agent is fed to the oxygen electrode instead of the oxygen-containing gas, i.e., feed of the oxygen-containing gas is terminated, and after lowering the cell voltage to the restoring voltage of the oxygen electrode (with respect to the fuel electrode), feed of the oxygen-containing gas is restarted.

In a still further preferred embodiment, the restoring operation contains such an operation that the load of the fuel cell is increased, and after lowering the cell voltage to the restoring voltage of the oxygen electrode (with respect to the fuel electrode), the load is decreased.

[0017]

In the method of the restoring operation by decreasing the feeding amount of oxygen, oxygen deficit occurs in a logical sense in the case where the utilization ratio of oxygen, i.e.,

four times the number of electrons flowing in the cell per the number of oxygen molecules fed to the cell, exceeds 100%, whereby the potential of the oxygen electrode is lowered. However, in an actual situation, even in the case where the utilization ratio is less than 100%, the potential of the oxygen electrode is lowered due to nonuniformity of gas feed and inhibition of gas diffusion to enable the restoring operation. The utilization ratio enabling the restoring operation is typically 70% or more while it varies depending on the constitution of the a gas flow path and the constitution of the gas diffusion layer. The utilization ratio can be increased by decreasing the feeding amount of oxygen, and the same effect can be obtained by increasing the load to increase the electric current flowing in the cell. In the case where the utilization ratio of oxygen is increased by increasing the electric current, the feeding amount of hydrogen should be increased in an amount corresponding to the electric current, so as to prevent the utilization ratio of hydrogen from being increased.

[0018]

In the method of the restoring operation by feeding a hydrocarbon gas, an inert gas or water for replacing oxygen, the oxygen partial pressure is decreased to lower the electric potential of the oxygen electrode.

Examples of the hydrocarbon gas include a city gas desulfurized with a desulfurizer, a propane gas and a butane

gas.

Examples of the inert gas include nitrogen, argon and carbon dioxide.

Water used herein may be in a vapor state or in a liquid state.

In the method of the restoring operation by feeding a reducing agent, the oxygen partial pressure is lowered by reacting oxygen with the reducing agent to lower the electric potential of the oxygen electrode. Furthermore, the deteriorated catalyst is reduced with the reducing agent to decompose contaminants. Examples of the reducing agent include a hydrogen gas, a sodium borohydride aqueous solution and hydrazine.

[0019]

In the method of the restoring operation by increasing the load of the fuel cell, the electric current flowing in the cell is temporarily increased to lower the cell voltage, whereby lowering the electric potential of the oxygen electrode. In a typical situation, while depending on the constitution of the cell and the constitution of the electrode, when the electric current is increased to 0.4 A per 1 cm^2 of the electrode area, the cell voltage becomes 0.7 V or less to enable the restoring operation.

[0020]

The restoring operation having been described in the

foregoing is carried out in such a state that a load is applied to the cell. However, although the efficiency is reduced, such an operation can also be employed that an inert gas, a hydrocarbon gas, water or a reducing agent is fed to the oxygen electrode in a state where the electric power generation is terminated, i.e., the load is detached, to effect the restoring operation of lowering the electric potential of the oxygen electrode, and then the operation of the fuel cell is terminated.

[0021]

An embodiment of the constitution of a fuel cell enabling the restoring operation according to the invention will be described with reference to Figs. 1 and 2.

A fuel cell 10 is constituted by alternately accumulating an MEA 11 and a separator plate 12. The MEA 11 is constituted with a polymer electrolyte membrane, a fuel electrode and an oxygen electrode sandwiching the electrolyte membrane, and a gasket sandwiching the electrolyte membrane at peripheries of the electrodes. The MEA 11 and the separator plate 12 each is provided with manifold holes 13 for an oxygen-containing gas, manifold holes 14 for a fuel gas and manifold holes 15 for cooling water. Fig. 1 shows only an electrode part of the MEA 11, and it is understood therefrom that air as the oxygen-containing gas fed from one of the manifold holes 13 of the separator plate 12 is fed to the oxygen electrode of the MEA through a gas flow path 16 and discharged to the outside

through the other of the manifold holes 13. A gas blocking means for closing an inlet of the gas flow path 16 is provided on the manifold hole 13 on the inlet side of the oxygen-containing gas as shown in Fig. 2. The gas blocking means is constituted with two screws 17, a plug body 18 screwed in the screws, and a means (not shown in the figure) for rotating the screws, and closes the inlet of the gas flow path 16 by sliding the plug body backward and forward in the manifold hole upon rotating the screws 17. The plug bodies are sequentially moved to enable the restoring operation for the respective cells by ones.

[0022]

A fuel cell system that is suitable for carrying out the restoring operation will be described.

In a preferred embodiment, as described in the foregoing, the fuel cell system comprising a stack of cells has a voltage detecting means for detecting a voltage of the cells or the stack, and a controlling means for controlling the feed of the oxygen-containing gas to the cells or the stack based on the voltage detected by the voltage detecting means.

In another preferred embodiment, the fuel cell system has a voltage detecting means for detecting a voltage of the cells or the stack, a feeding means for feeding an inert gas, a hydrocarbon gas, a reducing agent or water instead of the oxygen-containing gas to the cells or the stack, and a controlling means for controlling the feeding means based on

the voltage detected by the voltage detecting means.

In still another preferred embodiment, the fuel cell system has a voltage detecting means for detecting a voltage of the cells or the stack, an electric current adjusting means for increasing and decreasing an electric current applied to the cells or the stack, and a controlling means for controlling the electric current adjusting means based on the voltage detected by the voltage detecting means.

[0023]

Fig. 3 shows a schematic constitution of a fuel cell system having a controlling means for controlling the feed of the oxygen-containing gas to the cells or the stack. The fuel cell system 20 has a stack 21 formed by accumulating cells C_1, C_2, ... and C_n, a detecting device 29 connected to oxygen electrodes 23 of the respective electrodes and a fuel electrode 24 of the terminatory cell with lead wires for detecting voltages of the respective cells and the stack, and a controlling device 30 operated based on signals from the detecting device. Inlet ends of gas flow paths 25 for feeding the oxygen-containing gas to the oxygen electrodes 23 of the respective cells are connected to an inlet manifold 27 through switching valves A_1, A_2, ... and A_n, and outlet ends thereof are connected to an outlet manifold 28. A blower 26 feeds the oxygen-containing gas to the manifold 27. In the case where the detecting device 29 detects that the voltage of one or plural cells is lowered to

the threshold value or lower, the controlling device 30 controls the switching valve on the oxygen-containing gas feeding path to the one or plural cells to decrease the feeding amount of the oxygen-containing gas to the oxygen electrode, so as to attain the restoring operation. After restoring the voltage of the cell to the prescribed value, it is detected by the detecting device 29, and the switching valve is restored to the former state. The fuel gas feeding path and the load are omitted in Figure.

While the controlling device in this embodiment controls a resistance value of a resistor, it is possible that a relay or a transistor is used instead of the resistor, and the voltage of the cell to be restored is forcedly lowered.

[0024]

Fig. 4 shows a fuel cell system 40 according to another embodiment, which has the same constitution as in the system shown in Fig. 3 except that a controlling device 41 controls resistance values of resistors R_1, R_2, ... and R_n connected among the respective cells. In the fuel cell system of this embodiment, the cell voltage of the cell to be restored, e.g., C_1 herein, is forcedly lowered by shorting out the corresponding resistor R_1 by the signal from the detecting device 29, whereby the electric potential of the oxygen electrode of the cell C_1 is lowered to attain the restoring operation. Accordingly, the restoring operation can be attained sequentially for the

respective cells R_2, R_3, ... and R_n.

[0025]

EXAMPLES

The invention will be described in detail with reference to the following examples.

Example 1

An assembly of an electrolyte membrane and electrodes (MEA) was produced with a polymer electrolyte membrane and one pair of electrodes sandwiching the electrolyte membrane. A separator plate was produced with a graphite plate by cutting gas flow paths therein. The MEA was sandwiched with one pair of separator plates to fabricate a unit cell for measuring characteristics to conduct tests.

The temperature of the unit cell was set at 70°C. A hydrogen gas having been humidified to have a dew point of 70°C was fed to the fuel electrode, and air having been humidified to have a dew point of 70°C was fed to the oxygen electrode, whereby electric power generation was carried out at a fuel utilization ratio of 80%, an oxygen utilization ratio of 40%, and an electric current density of 200 mA/cm^2.

[0026]

In the case where the cell voltage was lowered to the threshold voltage value or lower, the electric power generation was continued under such a condition that air fed to the oxygen electrode was terminated, as the restoring operation, and after

lowering the cell voltage to the restoring electric potential, the feed of air was restarted. In this example, the threshold voltage value was 0.75 V, and the restoring electric potential of the oxygen electrode was 0.2 V per one cell (with respect to the fuel electrode). The period of time required from termination of air until the cell voltage is lowered to the restoring electric potential was about 10 seconds.

Fig. 5 shows the time-lapse change of the cell voltage in this example with the solid line. Fig. 6 shows the change of the cell voltage during the restoring operation. Fig. 5 also shows, as a comparative example, the time-lapse change of the cell voltage in the case of continuous operation of the cell without the restoring operation. It is understood in this example that a high cell voltage can be maintained in comparison to the comparative example.

[0027]

While the threshold voltage value in this example is 0.75 V, in the case where the threshold voltage value is set at a value higher than this value, the frequency of the restoring operation is increased to raise the average voltage. In the case where the threshold voltage value is set at a value lower than this value, on the other hand, the frequency of the restoring operation is decreased to lower the average voltage. The restoring operation in both cases can be carried out in the similar manner as in this example.

While the restoring electric potential of the oxygen electrode in this example was 0.2 V (with respect to the fuel electrode), the same effect was obtained when the restoring electric potential was changed within a range of from 0.1 to 0.4 V (with respect to the fuel electrode). While the restoring operation was carried out when the cell voltage was lowered to the threshold voltage value or lower in this example, the same effect can be obtained when the restoring operation is carried out after lapsing a prescribed period of time from the preceding restoring operation, for example, every 48 hours.

[0028]

Example 2

A unit cell was constituted in the same manner as in Example 1, and electric power generation was carried out in the same manner as in Example 1.

In the case where the cell voltage was lowered to the threshold voltage value or lower, the electric power generation was continued under such a condition that the feeding amount of air to the oxygen electrode was decreased, as the restoring operation, and after lowering the cell voltage to the restoring electric potential, the feeding amount of air was restored. In this example, the threshold voltage value was 0.75 V, and the restoring electric potential of the oxygen electrode was 0.2 V per one cell (with respect to the fuel electrode). The feeding amount of air upon the restoring operation was such

an amount that the oxygen utilization ratio was 100%, i.e., the value obtained by dividing four times the number of electrons flowing in the cell in a unit time by the number of oxygen molecules fed to the cell in a unit time was 100%.

[0029]

The period of time required from the decrease of the feeding amount of air until the cell voltage is lowered to the restoring electric potential was about 30 seconds. Fig. 7 shows the time-lapse change of the cell voltage in this example. A high cell voltage could be maintained similarly to Example 1. While the oxygen utilization ratio was 100% in this example, the same effect as in the case where the period of time until the cell voltage is lowered to the restoring electric potential was changed was obtained even in the case where the oxygen utilization ratio was changed from 70 to 120%.

[0030]

Example 3

60 of unit cells each having the same constitution as in Example 1 were accumulated to fabricate a stack. A fuel cell having the constitution described with reference to Figs. 1 and 2 was produced by using the stack. Electric power generation was carried out under the same conditions as in Example 1, and the restoring operation was carried out every 48 hours. The restoring operation was carried out in such a manner that electric power generation was continued under such

a condition that the feed of air to the cells of the stack was terminated one by one by using a gas blocking means provided in an air feeding manifold of the stack, and after the cell voltage of the cell, to which the feed of air had been terminated, was lowered to the restoring electric potential, the feed of air to the subsequent cell was terminated to restore the subsequent cell, whereby the cells were sequentially restored. The restoring electric potential of the oxygen electrode was 0.2 V (with respect to the fuel electrode) per one cell.

[0031]

Fig. 8 shows the time-lapse change of the voltage of the entire stack. Since the restoring operation was carried out for the respective cells constituting the stack in this example, the restoring operation of all the cells can be certainly completed, and the system using the fuel cell can be continuously operated because the voltage of the entire stack is not largely decreased even upon the restoring operation.

While the restoring operation is carried out by terminating the feed of air to every cell, the same effect can be obtained by terminating feed of air to plural cells to effect the restoring operation.

[0032

Example 4

A unit cell was constituted in the same manner as in Example 1, and electric power generation was carried out in the same

manner as in Example 1. As the restoring operation, the electric current was terminated, and nitrogen as the inert gas was fed to the oxygen electrode instead of air which had been fed to the oxygen electrode, and after lowering the cell voltage to the restoring electric potential, the feed of air was restarted. The threshold voltage value was 0.75 V, and the restoring electric potential of the oxygen electrode was 0.2 V per one cell (with respect to the fuel electrode). The feeding amount of nitrogen was the same as the feeding amount of air. Fig. 9 shows the time-lapse change of the cell voltage. A high cell voltage could be maintained as similar to Example 1.

While nitrogen is used as the inert gas in this example, the same effect is obtained by feeding a desulfurized city gas or water vapor. While the electric power generation is terminated upon the restoring operation in this example, the same effect is obtained when the electric power generation is continued.

[0033]

Example 5

A unit cell was constituted in the same manner as in Example 1, and electric power generation was carried out in the same manner as in Example 1. As the restoring operation, the electric current was terminated, and water was fed to the oxygen electrode instead of air which had been fed to the oxygen electrode, and after lowering the cell voltage to the restoring electric

potential, the feed of air was restarted. The threshold voltage value was 0.75 V, and the restoring electric potential of the oxygen electrode was 0.2 V per one cell (with respect to the fuel electrode). The feeding amount of water was the same as such an amount that fills the gas flow path of the cell. Fig. 10 shows the time-lapse change of the cell voltage. A high cell voltage could be maintained as similar to Example 1.

[0034]

Example 6

A stack was fabricated by accumulating 60 unit cells as similar to Example 3. Electric power generation was carried out under the same conditions as in Example 1, and the restoring operation was carried out every 48 hours. The restoring operation was carried out in such a manner that water was fed to every two cells in the stack by using a water feeding means provided in the air feeding manifold of the stack, and after the cell voltage of the cell, to which water had been fed, was lowered to the restoring electric potential (with respect to the fuel electrode), water was fed to the other cells to restore them, whereby the cells were sequentially restored. The restoring electric potential of the oxygen electrode was 0.2 V (with respect to the fuel electrode) per one cell.

[0035]

The water feeding means was constituted in such a manner that a water feeding pipe 19 was provided as shown in Fig. 1,

and water was poured from the pipe to the gas flow paths 16 of the adjacent two cells through the manifolds. Fig. 11 shows the time-lapse change of the voltage of the entire stack. According to this example, the restoring operation could be carried out without large decrease of the voltage of the entire stack as similar to Example 3.

[0036]

Example 7

A unit cell was constituted in the same manner as in Example 1, and electric power generation was carried out in the same manner as in Example 1. As the restoring operation, the electric current was terminated, and aqueous solution containing 1% of a sodium borohydride was fed to the oxygen electrode instead of air which had been fed to the oxygen electrode, and after lowering the cell voltage to the restoring electric potential (with respect to the fuel electrode), the feed of air was restarted. The threshold voltage value was 0.75 V, and the restoring electric potential of the oxygen electrode was 0.2 V per one cell (with respect to the fuel electrode). The feeding amount of the aqueous solution was the same as such an amount that fills the gas flow path of the cell.

Fig. 12 shows the time-lapse change of the cell voltage in this example. A high cell voltage could be maintained as similar to Example 1. While a sodium borohydride aqueous solution is used in this example, the same effect is obtained

by feeding an aqueous solution containing hydrazine instead.

[0037]

Example 8

A unit cell was constituted in the same manner as in Example 1, and electric power generation was carried out in the same manner as in Example 1. As the restoring operation, electric power generation was continued by increasing twice the feeding amount of hydrogen and increasing twice the electric current every 24 hours, and after 30 seconds, the feeding amount of hydrogen and the electric current were restored. Upon the restoring operation, the cell voltage was temporarily lowered to 0.6 V. Fig. 13 shows the time-lapse change of the cell voltage in this example. A high cell voltage could be maintained as similar to Example 1.

[0038]

Example 9

A unit cell was constituted in the same manner as in Example 1, and electric power generation was carried out in the same manner as in Example 1. Every 12 hours, the electric current was terminated, and nitrogen as the inert gas was fed to the oxygen electrode instead of air which had been fed to the oxygen electrode. After lowering the cell voltage to the restoring electric potential (with respect to the fuel electrode), the feed of hydrogen to the hydrogen electrode was terminated, and nitrogen was also fed to the hydrogen electrode to effect purge.

Thereafter, the feed of gases to both the electrodes was terminated. The cell was cooled to room temperature in a forced manner or by standing. After 12 hours from the termination of the operation, the feed of hydrogen and air was restarted under heating the cell to 70°C, so as to restart electric power generation. Upon repeating the foregoing procedures, a high cell voltage could be maintained. Fig. 14 shows the time-lapse change of the cell voltage in this example.

[0039]

[Effects of the Invention]

According to the invention as described in the foregoing, the high generation effeciency is maintained for a long period of time by carrying out a restoring operation for restoring the generated voltage by decreasing the electric potential of the oxygen electrode upon decreasing of the generated voltage of the fuel cell.

[Brief Description of the Drawings]

Fig. 1 is an elevational view showing an embodiment of the invention, where a part of a stack is removed.

Fig. 2 is a cross sectional view of the embodiment shown in Fig. 1 on line II-II'.

Fig. 3 is a diagram showing a schematic constitution of a fuel cell system of another embodiment of the invention.

Fig. 4 is a diagram showing a schematic constitution of a fuel cell system of still another embodiment of the invention.

Fig. 5 is a graph showing time-lapse changes of cell voltages in Example 1 and a comparative example.

Fig 6 is a graph showing behavior of a cell voltage on a restoring operation in Example 1.

Fig. 7 is a graph showing a time-lapse change of a cell voltage in Example 2.

Fig. 8 is a graph showing a time-lapse change of a stack voltage in Example 3.

Fig. 9 is a graph showing a time-lapse change of a cell voltage in Example 4.

Fig. 10 is a graph showing a time-lapse change of a cell voltage in Example 5.

Fig. 11 is a graph showing a time-lapse change of a stack voltage in Example 6.

Fig. 12 is a graph showing a time-lapse change of a cell voltage in Example 7.

Fig. 13 is a graph showing a time-lapse change of a cell voltage in Example 8.

Fig. 14 is a graph showing a time-lapse change of a cell voltage in Example 9.

[Explanations of Reference Numbers]

10 fuel cell

11 MEA

12 separator plate

13 manifold hole for an oxygen-containing gas

14 manifold hole for a fuel gas

15 manifold hole for cooling water

16 gas flow path

17 screw

18 plug body

19 water feeding pipe

20 fuel cell system

21 stack

23 oxygen electrode

24 fuel electrode

25 gas flow path

26 blower

27 inlet manifold

28 outlet manifold

29 detecting device

30,41 controlling device

40 fuel cell system

A_1,A_2,A_n switching valve

C_1,C_2,C_n cell

R_1,R_2,R_n resistor

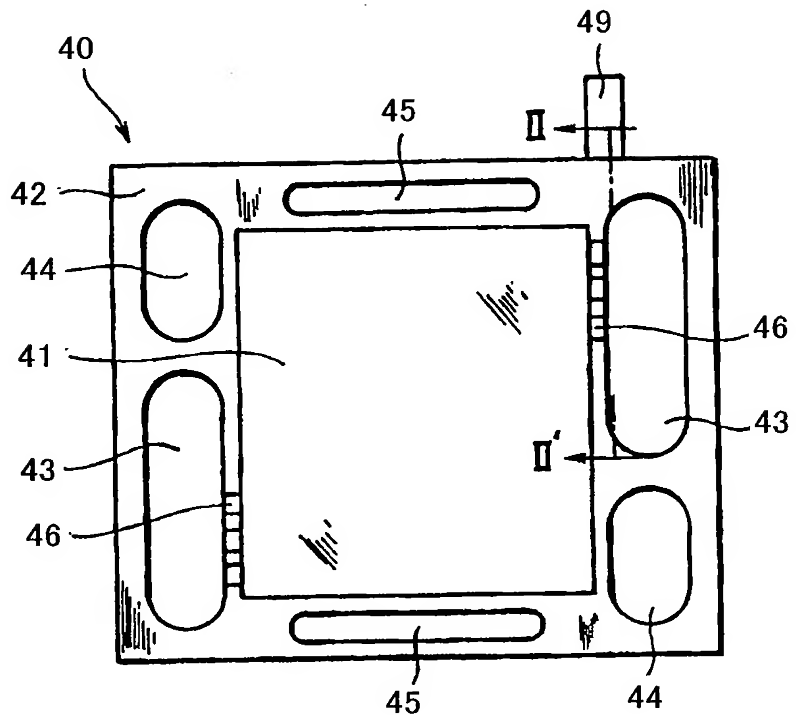


FIG. 1

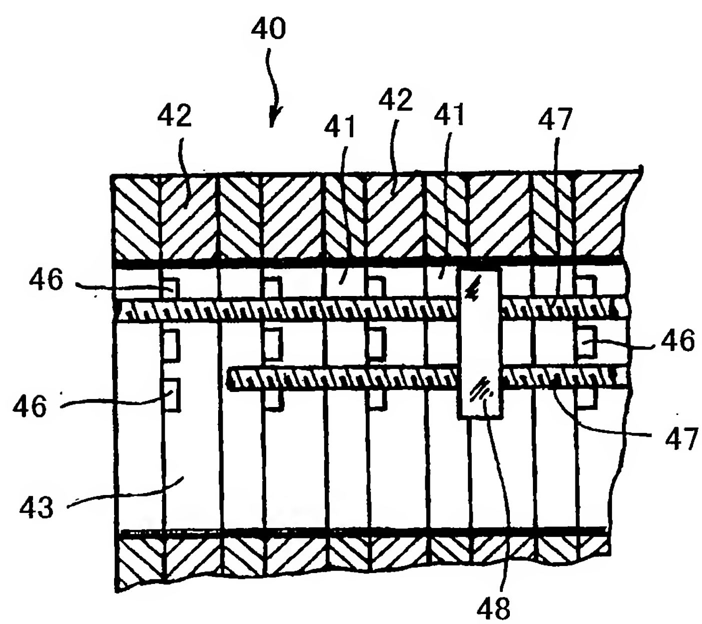
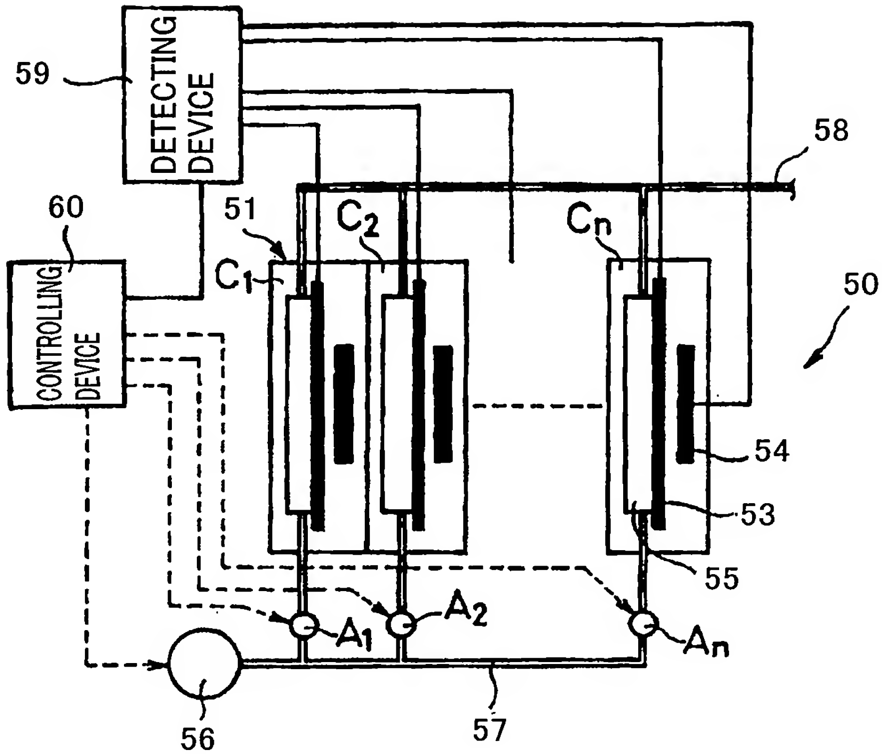


FIG. 2



DETECTING DEVICE
CONTROLLING DEVICE
59
60
58
51
50
C1
C2
Cn
54
53
55
A1
A2
An
56
57

FIG. 3

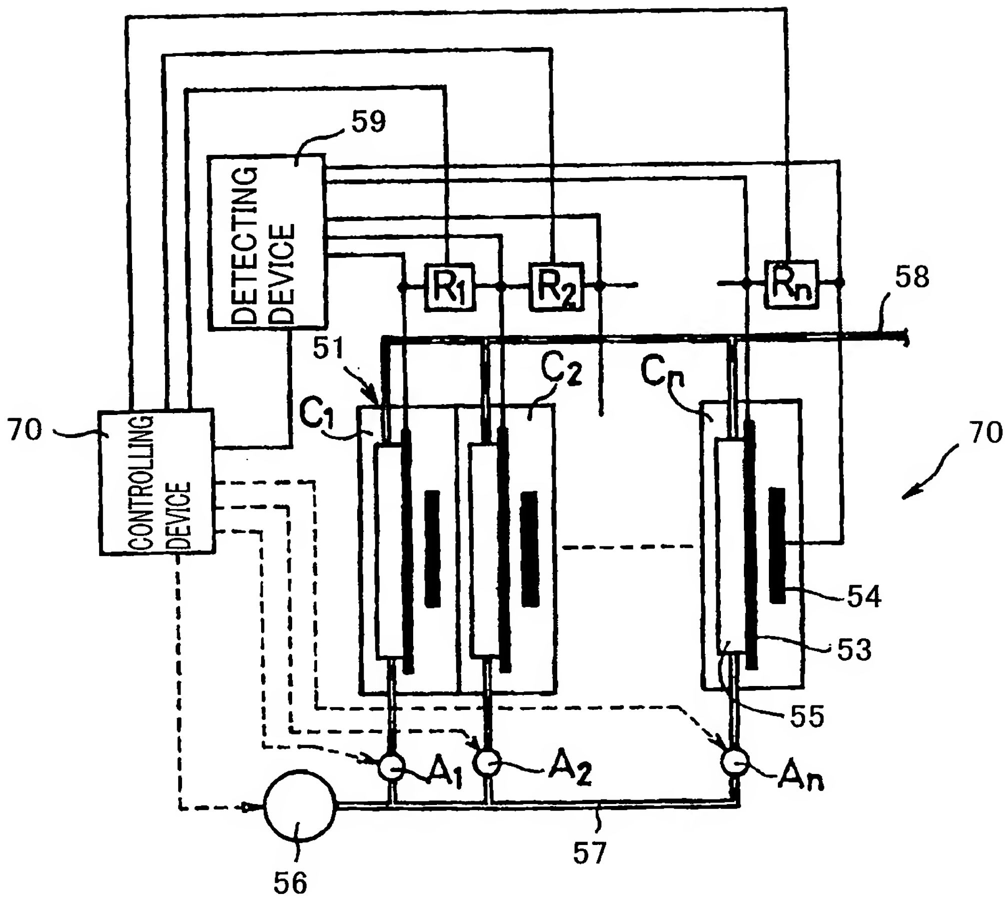

59
DETECTING DEVICE
R1
R2
Rn
58
51
C2
Cn
C1
70
CONTROLLING DEVICE
70
54
53
55
A1
A2
An
57
56

FIG. 4

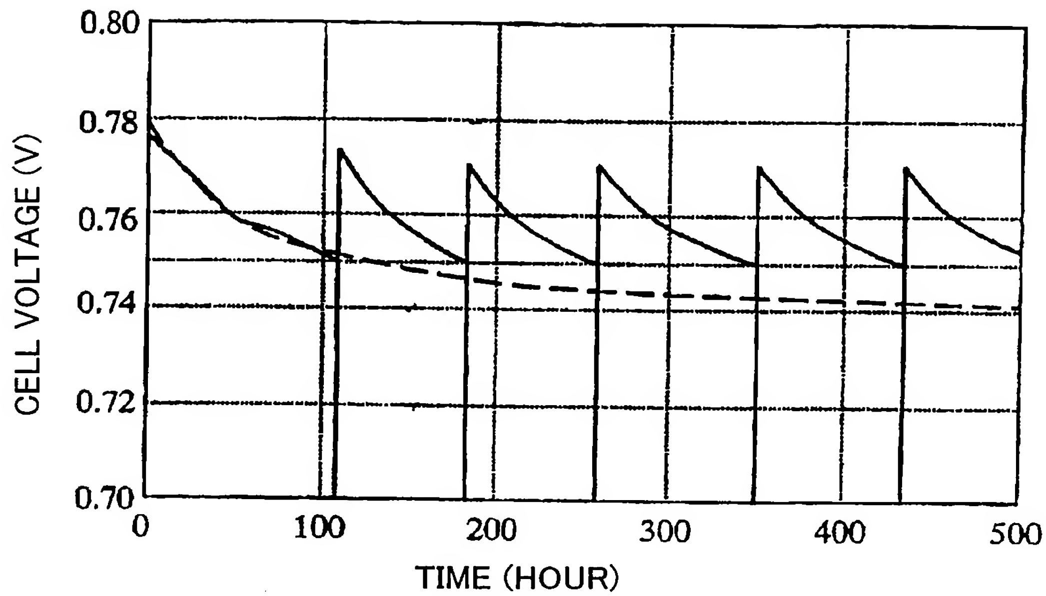

0.80
0.78
0.76
0.74
0.72
0.70
CELL VOLTAGE (V)
0
100
200
300
400
500
TIME (HOUR)

FIG. 5

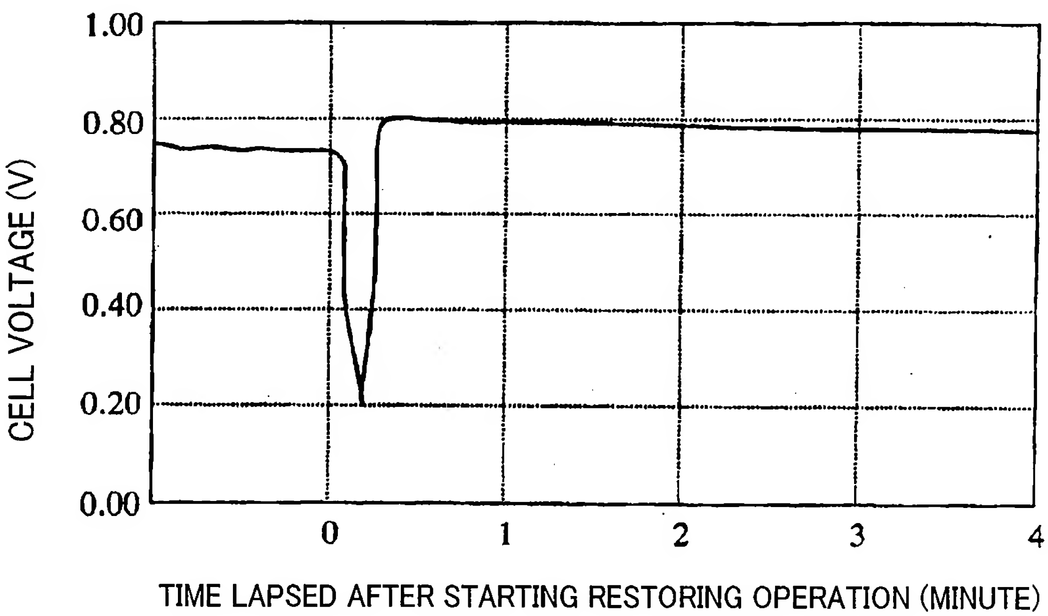

1.00
0.80
0.60
0.40
0.20
0.00
CELL VOLTAGE (V)
0
1
2
3
4
TIME LAPSED AFTER STARTING RESTORING OPERATION (MINUTE)

FIG. 6

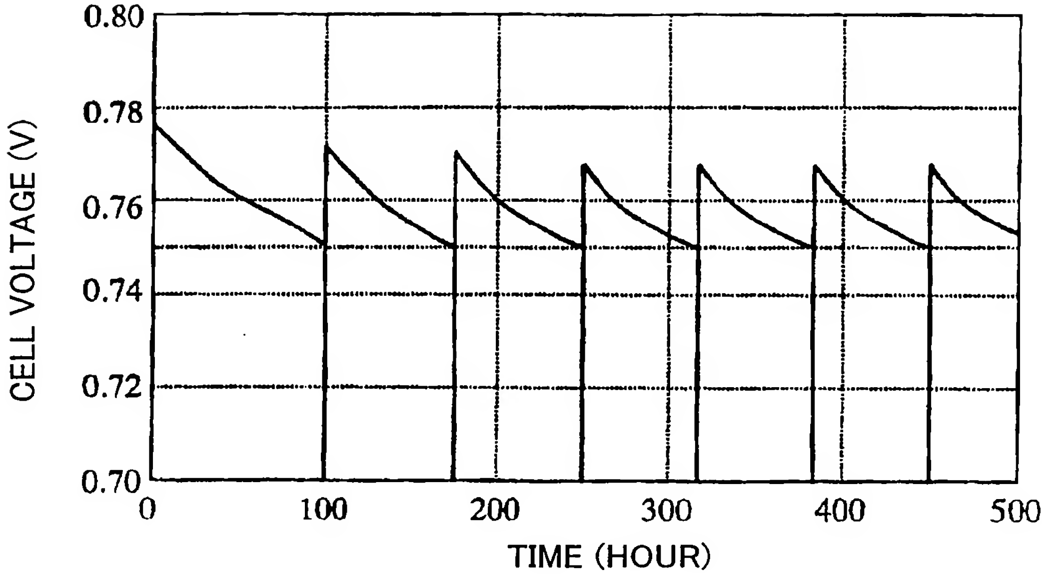

0.80
0.78
0.76
0.74
0.72
0.70
CELL VOLTAGE (V)
0
100
200
300
400
500
TIME (HOUR)

FIG. 7

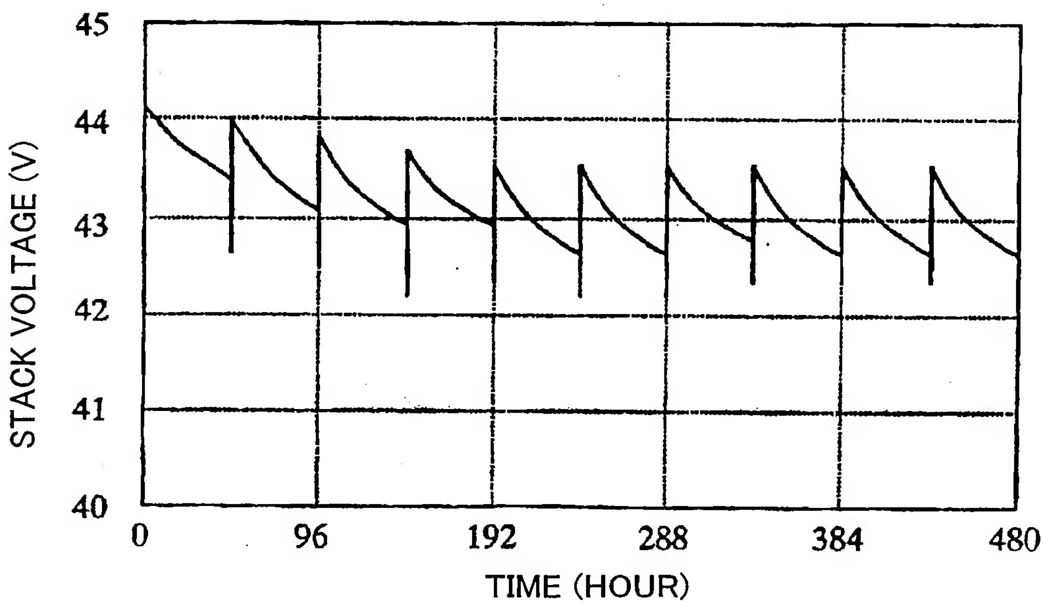

45
44
43
42
41
40
STACK VOLTAGE (V)
0
96
192
288
384
480
TIME (HOUR)

FIG. 8

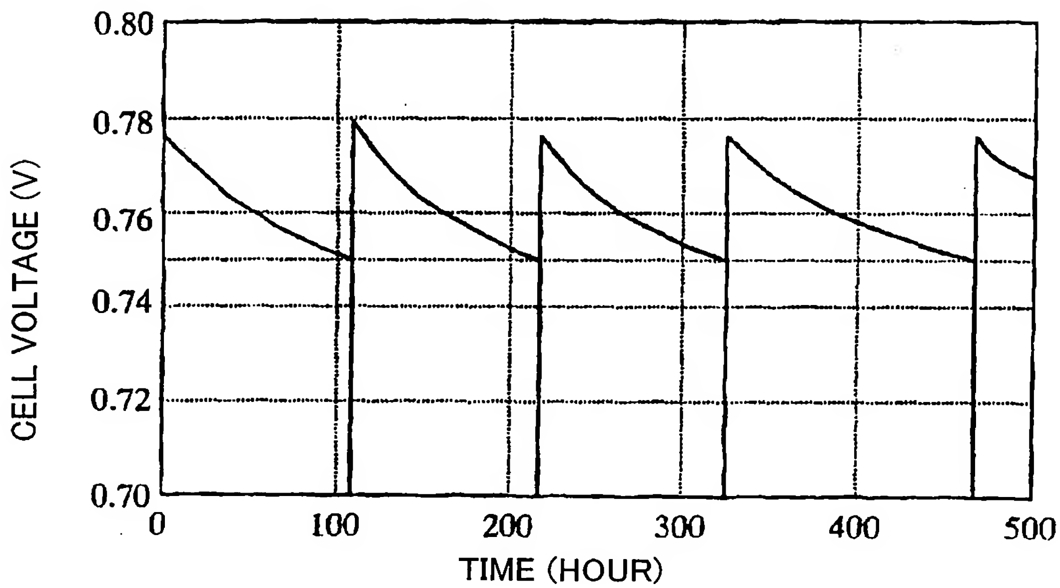

0.80
0.78
0.76
0.74
0.72
0.70
CELL VOLTAGE (V)
0
100
200
300
400
500
TIME (HOUR)

FIG. 9

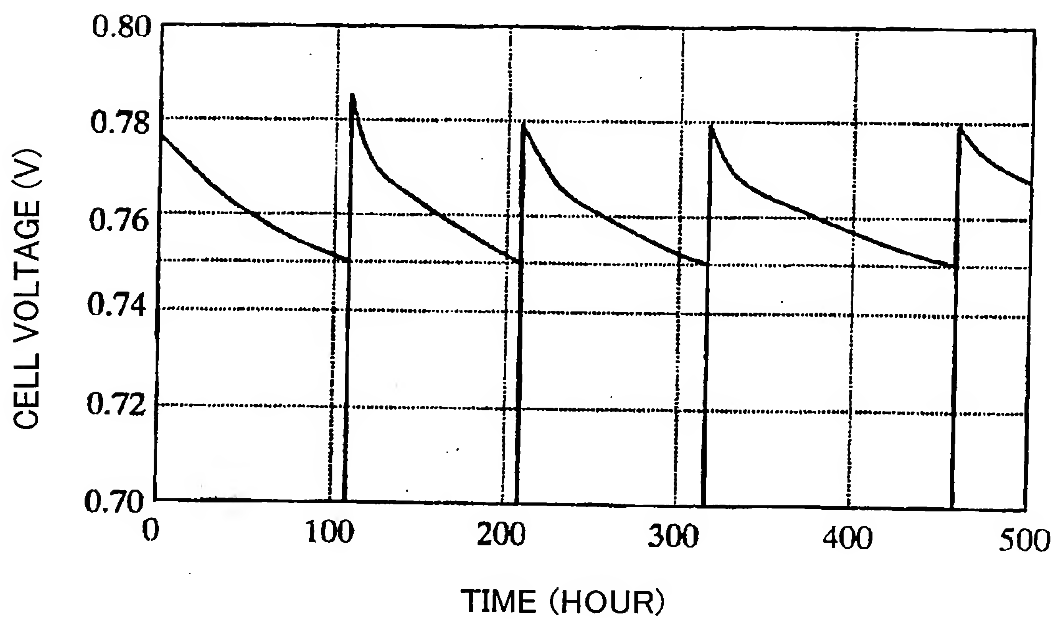

0.80
0.78
0.76
0.74
0.72
0.70
CELL VOLTAGE (V)
0
100
200
300
400
500
TIME (HOUR)

FIG. 10

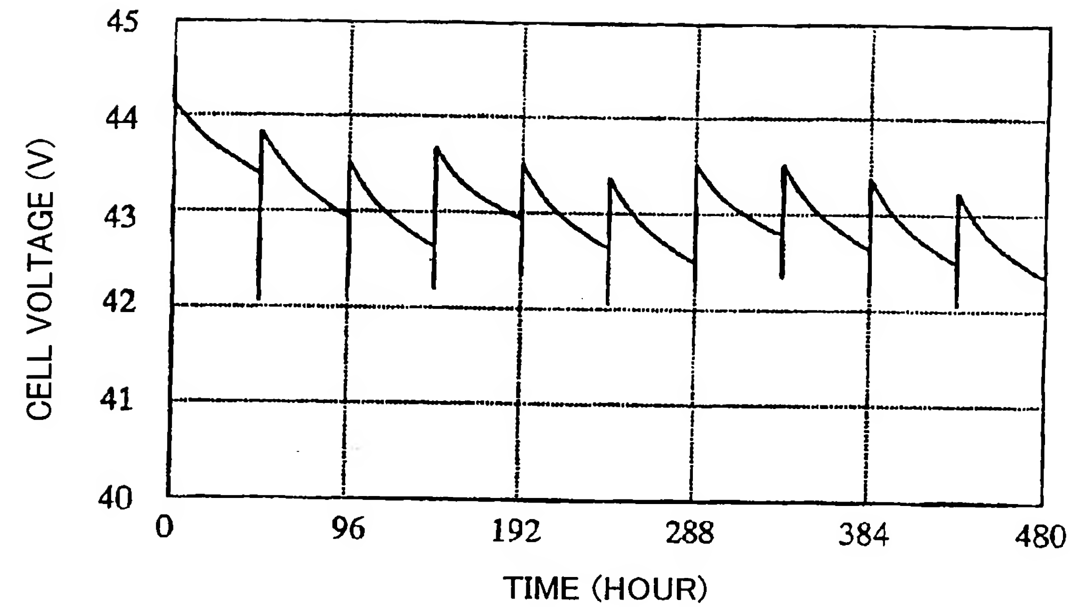

45
44
43
42
41
40
CELL VOLTAGE (V)
0
96
192
288
384
480
TIME (HOUR)

FIG. 11

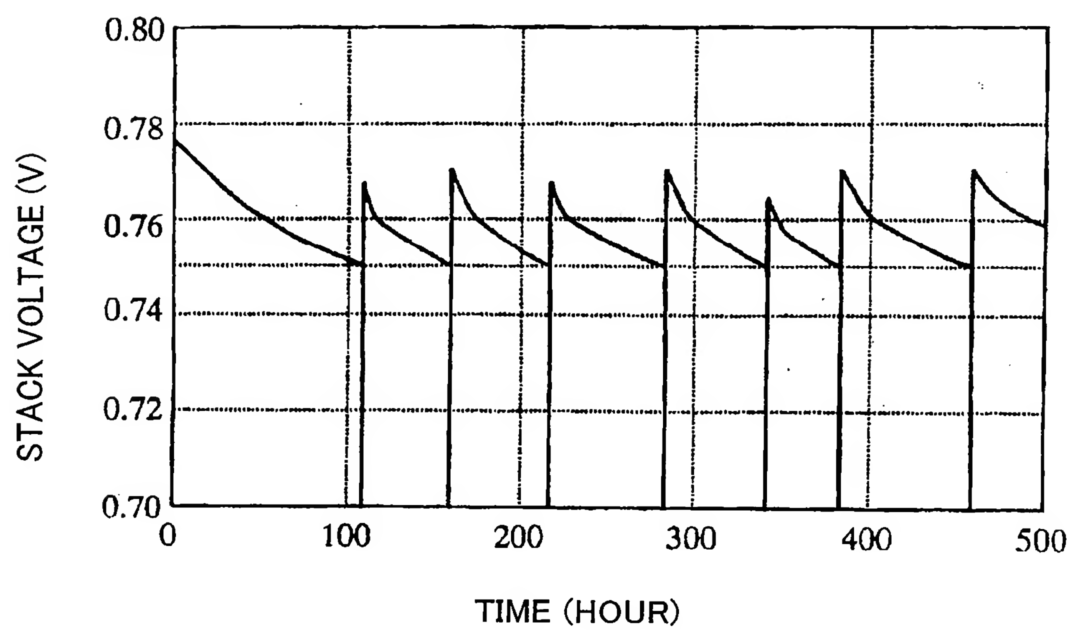

0.80
0.78
0.76
0.74
0.72
0.70
STACK VOLTAGE (V)
0
100
200
300
400
500
TIME (HOUR)

FIG. 12

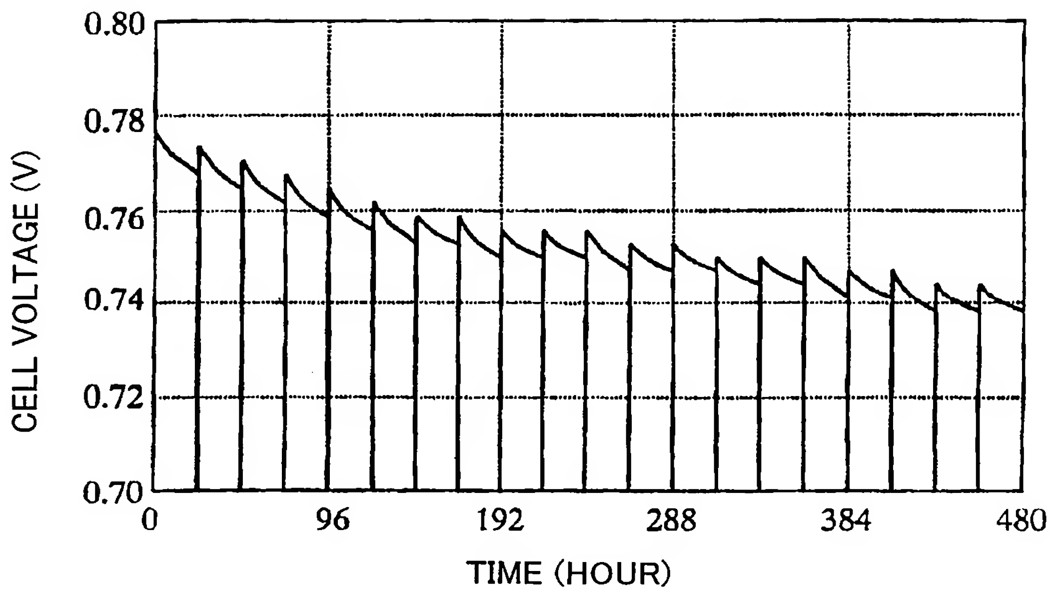

0.80
0.78
0.76
0.74
0.72
0.70
CELL VOLTAGE (V)
0
96
192
288
384
480
TIME (HOUR)

FIG. 13

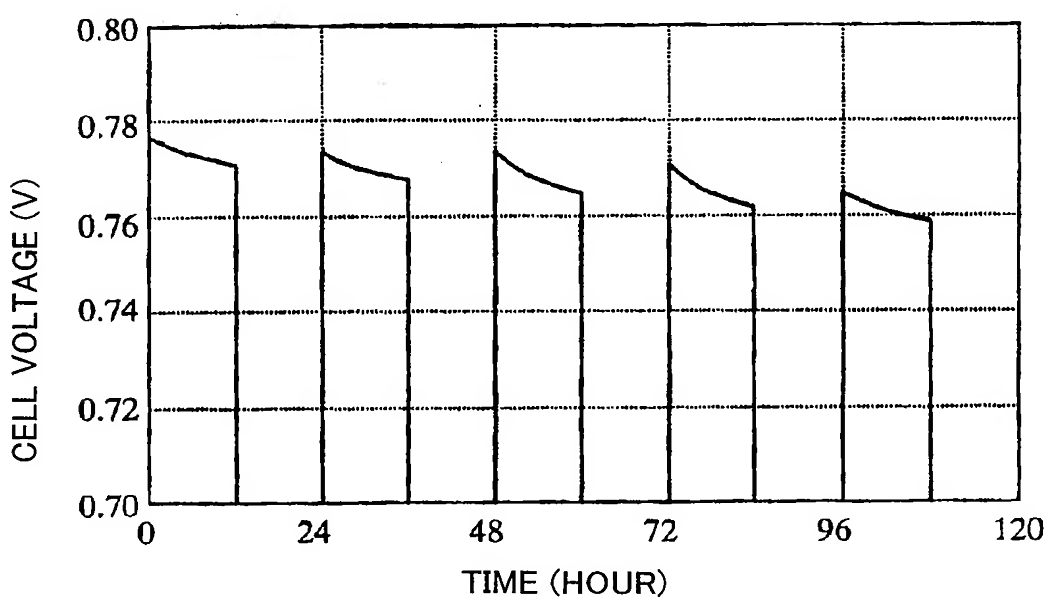

0.80
0.78
0.76
0.74
0.72
0.70
CELL VOLTAGE (V)
0
24
48
72
96
120
TIME (HOUR)

FIG. 14

ABSTRACT OF THE DISCLOSURE

[Name of Document] Abstract

[Abstract]

[Problem] An object is to provide a method for operating a fuel cell for maintaining a high generated voltage for a long period of time by carrying out a restoring operation for restoring the generated voltage upon decreasing the generated voltage of the fuel cell.

[Means for Solving the Problem] The method is for operating a fuel cell containing an electrolyte, one pair of electrodes sandwiching the electrolyte, and one pair of separator plates each having a gas flow path for feeding and discharging a fuel gas to one of the electrode and for feeding and discharging an oxygen-containing gas to the other electrode, and the method contains a step of carrying out a restoring operation for decreasing an electric potential of the electrode on an oxygen side by carrying out the electric power generation continuously while decreasing the feed of the oxygen-containing gas to the oxygen electrode, upon decreasing of a voltage of one or more specific cells to a threshold voltage or lower. Thereby, the generated voltage is restored.

[Selected Drawing] Fig. 3